Environmental Health Perspectives
Vol. 19, pp. 1–4, 1977

Applications of Arsine Evolution Methods to Environmental Analyses

by Robert S. Braman*

Because of its biological activity, arsenic is involved in an active global geochemical cycle. Arsenic has been found to be transferred to the atmosphere, at least in part, by evolution of trimethyl arsine and similar methyl arsenic compounds. Because of the environmental importance of the several arsenic forms [inorganic arsenic (III) and (V), methylarsonic acid, dimethylarsenic acid, trimethylarsine, methylarsine, and dimethylarsine], chemical methods for their analysis are needed. Sensitive methods are required because environmental concentrations encountered are generally in the range of 0.01 (or lower) to 3 ppb for natural waters and 1–6 ng As/m^3 for arsenic in air. Arsine evolution by pH selective reduction permits specific analyses for inorganic As (III) and As (V). Methylarsenic acids may be reduced to corresponding methylarsines with sodium borohydride after which separation permits specific detection of these arsenic compounds. The most sensitive and selective methods combine reduction, separation, and emission type detectors. The intensity of arsenic atomic emission lines is observed. This type of detector provides a lower limit of detection down to 0.02 ng As per sample. The methods have been applied to a variety of environmental samples.

The Analytical Problem

Except for specific ore deposits, arsenic is generally a trace element present in soils and rocks usually in the low parts-per-million range. Higher concentrations of arsenic are found in sedimentary rocks because of its tendancy to coprecipitate with metal hydroxides, carbonates, and silicates in natural sedimentation processes. Natural fresh waters contain generally less than 1 ppb arsenic, while the sea water content is on the order of 3 ppb despite its removal by sedimentation. Arsenic is involved in a global cycle which includes volatile arsenic compounds.

Because of its biological activity one finds methylarsenic type compounds in the environment; methylarsonic acid, dimethylarsinic acid, their acid salts, trimethylarsine, and trimethylarsine oxide. The methylarsenic compounds are generally present only in low concentrations compared to inorganic forms. Nevertheless, in certain locations in the environment exhibiting high biological activity, the methylarsenic compounds may be present in higher concentration than the inorganic compounds. This has been found to be true for some small lakes or ponds. Even so, concentrations of these methylarsenic compounds rarely exceed 10 ppb. Methylarsenic compounds may be present in samples as a result of the use of arsenic pesticides or silvicides or as a consequence of biomethylation. Biological activity can readily convert methylarsenic compounds to higher methylated forms and to methylarsines.

Ambient air in comparatively nonpolluted locations contains on the average 4–6 ng As/m^3. In certain polluted urban locations this rises to 10–20 ng As/m^3 or more. Most airborne arsenic particulate consists of inorganic arsenic (III) compounds. Some arsenic (V) compounds are also present. In areas of substantial biological activity and/or arsenic pollution, the methylarsines or methylarsenic acid type compounds may also be found.

Biota appear to concentrate arsenic somewhat. Some aquatic animals contain up to 100 ppm arsenic. Much of this is likely one of the biomethylated forms of arsenic.

The environmental analyst is, therefore, faced with a substantial problem in the development of methods for arsenic. Methods must be available for analyzing arsenic in the 1–10 ng range if ambient air

*Department of Chemistry, University of South Florida, Tampa, Fla. 33620.

or natural waters are to be analyzed. Soil, rocks, minerals, sediments, and biota will generally involve analyses of larger amounts or arsenic per sample, but sample treatment becomes more of a problem.

Although most analyses have been for total arsenic, this type of analysis is not sufficient for environmental work if details of the arsenic chemistry are to be studied.

Chemistry of Arsine Generation

Separation of arsenic from interfering sample matrix materials by converting it to arsine has long been used as a first step in arsenic analyses. Two approaches have been used. Reduction of arsenic in acidic media by active metals such as zinc or magnesium is the classical approach. Reduction in solution by sodium borohydride has more recently been employed; it is apparently more rapid than some zinc reduction methods which require up to 90 min for reduction. It is also less subject to interference from traces of arsenic in the zinc reagent. Griffin et al. (*1*), for example, report that they found the zinc used for reduction contained 80 ppb As. Blank values for the 5 g samples of zinc in the reduction gave a 150 ng blank. This is intolerable for most environmental analyses.

Methylarsenic compounds and inorganic arsenic acids are all reduced to the corresponding arsine or methylarsine by both active metals and by sodium borohydride. This reduction process is pH-dependent. The several arsenic acid compounds must be in the undissociated state for the reduction to proceed at an appreciable rate. This pH dependency permits specific reduction of some of the arsenic acids in the presence of others. For example, arsenious acid (pK 9.23) may be reduced to arsine in the pH 4–9 range, while arsenic acid is not (pK_{a1} 2. 25). Thus, arsenic (III) may be determined in the presence of arsenic (V).

Arsine Analysis Methods

After arsine evolution, the finishing analytical method may be one of several types. The most popular, because of its simplicity, is colorimetric determination of the complex arsine with silver diethyldithiocarbamate. This method has poor precision for sample sizes below 1 μg and consequently is not suitable for most environmental work except monitoring for arsenic above 10–20 ppb concentration. Methylarsenic compounds complicate the analysis method. Methylarsinic acid and dimethylarsinic acid both reduced to the methylarsines by zinc form colored complexes with silver diethyldithiocarbamate. These complexes have different molar absorptivities than that of the arsine complex. Absorption maxima are shifted to the red, but overlap. The difference in the absorption spectra has been used as an approach to the determination of methylarsenic compounds by Peoples et al. (*2*). A colorimetric method for the simultaneous determination of inorganic arsenic, methylarsenic compounds, and dimethylarsenic compounds is theoretically possible, but sensitivity of colorimetric methods is too poor for most environmental applications.

Atomic absorption detection of arsenic after conversion to arsine gives far better lower limits of detection than the colorimetric method and has the advantage that it can be automated (*3, 4*). Holak (*5*), Dalton and Malonski (*6*), and Fernandez and Manning (*7*) were among the first to employ this approach using an argon/hydrogen flame. Chu et al. (*8*) found that if arsine is thermally decomposed in a flameless atomic absorption approach, the limit of detection is reduced by a factor of two. Limits of detection reported are quite variable. Flame methods appear to have a limit of detection near 40 ng per sample or 5 ppb on a concentration basis (*1, 5–8*). Flameless methods are substantially more sensitive (*8*); limits of detection down to 1 ng are reported with a graphite resistance furnace (*9*). It would appear that combination of a cold trapping arsine collection method with a properly designed and controlled high temperature furnace for decomposing arsines will, in the case of atomic absorption detection, have sufficient sensitivity for environmental analyses.

The generation of methylarsines from samples containing the appropriate arsenic compounds may constitute a problem. The high temperature furnace would have to atomize the methyl arsines completely. Background absorption may also be a problem.

The best lower limits of detection are exhibited by the emission detection methods. Using a microwave-stimulated plasma discharge in argon and reduction by zinc, Lichte and Skogerboe (*10*) obtained a limit of detection of 5 ng (2.5 ppb for 2 ml samples). This limit of detection was attributed largely to the blank content of arsenic in the zinc.

Using a dc discharge in helium with reduction by sodium borohydride in a continuous analysis method (no cold trapping), Braman, Justen, and Foreback (*11*) obtained a lower limit of detection of 1 ng (0.1 ppb, 10 ml samples). When a liquid nitrogen cooled U-trap is used, the limits of detection improved to 0.2 ng (0.002 ppb, 100 ml samples) with the dc discharge method (*12, 13*).

The microwave stimulated plasma detector combined with gas chromatographic separation of the arsines in the method of Talmi and Bostick (*14*) exhibits a lower limit of detection of 0.02 ng. Arsines are trapped in 5 ml of cold toluene, 10 μl of which are separated on the gas chromatograph. Unfortunately, since only a small fraction of the original sample is analyzed, the concentration limit of detection is only on the order of 1 ppb.

Separation of the methylarsines and arsine prior to detection permits determination of the methylarsenic acids. Conventional gas chromatography separation followed by emission detection was used in the method of Talmi and Bostick (*14*).

A less complex separation method has been developed by Braman and Foreback (*12, 13*). Arsines evolved after reduction by sodium borohydride are trapped on a liquid nitrogen-cooled U-tube packed with 60–80 mesh glass beads. After removal of the liquid nitrogen and gentle warming of the U-tube, the arsines are evolved out of the trap one at a time and are detected in the dc discharge. Excellent separation of the arsines is obtained with limits of detection near 0.5 ng (0.005 ppb, 100 ml samples) for the methylarsines. The finding of the methylarsenic compounds in a number of different environmental samples using this technique points to the need for speciation analyses of arsenic (*12, 15*).

Sample Treatment

Oxidation is generally employed when biological type samples are to be prepared for analysis. Most procedures involve the us of large amounts of such oxidizing materials as sulfuric acid, nitric acid, perchloric acid, and hydrogen peroxide. Care must be exercised so as to avoid losses of arsenic during heating. Experience of this writer with such procedures is that the oxidizing chemicals contain unacceptably large amounts of arsenic. The oxidation procedures are probably acceptable if the finishing method is by colorimetry.

Samples of biological materials homogenized in a blender with mild sodium hydroxide solution (0.05*M*) can be analyzed by subsequent treatment with sodium borohydride (*15*). Arsenic compounds appear to be satisfactorily reduced to the arsines. Oxidation cannot be used if the methylarsenic compounds must be determined.

Air at the ambient arsenic concentration, 4–6 ng As/m^3, has been analyzed for the several environmental forms in a two-stage sampling system (*16*). Glass wool filters which have a low arsenic blank (1 ng or less) were used to collect the particulate. A silver-coated glass bead column was used below the filter to collect the volatile arsines if present. The silver-coated beads collect arsines quantitatively; they are oxidized in the process of removal by washing with 0.05*M* sodium hydroxide to the methylarsenic acids which may then be analyzed. The particulate phase may be analyzed by homogenizing the filters in a 0.05*M* sodium hydroxide and then using the sodium borohydride reduction method. Detectable amounts of the methylarsines were found in air above soil treated with arsenic compounds (*17*) and in commercial greenhouses (*16*).

Future Problem Areas

Although substantial progress has been made in the development of methods for environmental analysis, the analysis of sediments and particulate for specific inorganic arsenic compounds remains unsolved. The identification of organic arsenic compounds other than the simple methylarsenic types also is a potential problem. Much more application work in the analysis for methylarsenic and inorganic arsenic compounds needs to be done.

REFERENCES

1. Griffin, H. R., Hocking, M. B., and Lowrey, D. G. Arsenic determination in tobacco by atomic absorption spectrometry. Anal. Chem., 47: 229 (1975).
2. Peoples, S. A., Lakso, J., and Lais, T. Proc. West. Pharmacol. Soc., 14: 178 (1971).
3. Pierce, F. D., et al. Appl. Spectroscopy, (Jan.-Feb. 1976).
4. Pierce, F. D., and Brown, H. R. Inorganic interference study of automated arsenic and selenium determination with atomic absorption spectrometry. Anal. Chem. 48: 693 (1976).
5. Holak, W. Gas-sampling technique for arsenic determination by atomic absorption spectrophotometry. Anal. Chem., 41: 1712 (1969).
6. Dalton, E. F., and Malonoski, A. J. Atomic Absorption Newslett., 10: 92 (1971).
7. Fernandez, F. J. and Manning, D. C. Atomic Absorption Newslett., 10: 36 (1971).
8. Chu, R. C., Barron, G. P., and Baumgarner, P. A. W. Arsenic determination at sub-microgram levels by arsine evolution and flameless atomic absorption spectrophotometric technique. Anal. Chem. 44: 1476 (1972).
9. Knudson, E. J., and Christian, G. D. Flameless atomic absorption determination of volatile hydrides using cold trap collection. Anal. Lett., 6: 1039 (1973).
10. Lichte, F. E., and Skogerboe, R. K. Emission spectrometric determination of arsenic. Anal. Chem. 44: 1480 (1972).
11. Braman, R. S., Justen, L. L., and Foreback, C. C. Direct volatilization spectral emission type detection system for nanogram amounts of arsenic and antimony. Anal. Chem., 44: 2195 (1972).
12. Braman, R. S. and Foreback, C. C. Methylated forms of arsenic in the environment. Science 182: 1247 (1973).
13. Foreback, C. C. Some studies on the detection and determination of mercury, arsenic and antimony in gas discharges. Ph.D. Thesis, University of South Florida, Tampa, Florida, 1973.

14. Talmi, Y., and Bostick, D. T. Determination of alkylarsenic acids in pesticide and environmental samples by gas chromatography with a microwave emission spectrophotometric detection system. Anal. Chem. 47: 2145 (1975).
15. Johnson, D. L., and Braman, R. S. The spectation of arsenic and the content of germanium and mercury in members of the Pelagic Sargassum community. Deep-Sea Res. 22: 503 (1975).
16. Johnson, D. L., and Braman, R. S. Alkyl- and inorganic arsenic in air samples. Chemosphere, 6: 333 (1975).
17. Braman, R. S. Arsenic in the environment. In: Arsenical Pesticides (ACS Symp. Ser., 7), E. A. Woolson, Ed., American Chemical Society, Washington, D. C., 1975.